



## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<b>(51) International Patent Classification <sup>6</sup> :</b> <b>A61K 7/00, C11D 17/00</b>	<b>A1</b>	<b>(11) International Publication Number:</b> <b>WO 97/17938</b> <b>(43) International Publication Date:</b> 22 May 1997 (22.05.97)
<b>(21) International Application Number:</b> PCT/EP96/04172 <b>(22) International Filing Date:</b> 20 September 1996 (20.09.96) <b>(30) Priority Data:</b> 9523167.6 13 November 1995 (13.11.95) GB <b>(71) Applicant (for AU BB CA GB IE IL KE LC LK LS MN MW NZ SD SG SZ TT UG only):</b> UNILEVER PLC [GB/GB]; Unilever House, Blackfriars, London EC4P 4BQ (GB). <b>(71) Applicant (for all designated States except AU BB CA GB IE IL KE LC LK LS MN MW NZ SD SG SZ TT UG):</b> UNILEVER N.V. [NL/NL]; Weena 455, NL-3013 AL Rotterdam (NL). <b>(72) Inventors:</b> GOEL, Satish, Kumar; 1A Agrasar, Hindustan Lever Research Centre Flats, ICT Link Road, Andheri East, Bombay, Maharashtra-400099 (IN). SANKHOLKAR, Devadatta, Shivaji; Hindustan Lever Research Centre Flats, ICT Link Road, Andheri East, Bombay, Maharashtra- 400099 (IN). <b>(74) Agent:</b> ELLIOTT, Peter; Unilever plc, Patent Division, Col- worth House, Sharnbrook, Bedford MK44 1LQ (GB).		<b>(81) Designated States:</b> AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, HU, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, TJ, TM, TR, TT, UA, UG, UZ, VN, ARIPO patent (KE, LS, MW, SD, SZ, UG), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).  <b>Published</b> <i>With international search report.</i> <i>Before the expiration of the time limit for amending the</i> <i>claims and to be republished in the event of the receipt of</i> <i>amendments.</i>
<b>(54) Title:</b> THREE-PHASE EMULSION COSMETIC COMPOSITION  <b>(57) Abstract</b>  A three-phase emulsion system is provided which comprises from 2 % to 30 % by wt. emulsifier; from 20 % to 80 % by wt. of one or more oil-based functional ingredients; from 20 % to 80 % by wt. silicone oil; and from 0.1 % to 30 % by wt. water. The emulsion is in a water continuous or oil-continuous form. The composition is such that loss of functional ingredients in a wash situation is minimized and that the emulsions have enhanced occlusive properties.		

**FOR THE PURPOSES OF INFORMATION ONLY**

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AM	Armenia	GB	United Kingdom	MW	Malawi
AT	Austria	GE	Georgia	MX	Mexico
AU	Australia	GN	Guinea	NE	Niger
BB	Barbados	GR	Greece	NL	Netherlands
BE	Belgium	HU	Hungary	NO	Norway
BF	Burkina Faso	IE	Ireland	NZ	New Zealand
BG	Bulgaria	IT	Italy	PL	Poland
BJ	Benin	JP	Japan	PT	Portugal
BR	Brazil	KE	Kenya	RO	Romania
BY	Belarus	KG	Kyrgyzstan	RU	Russian Federation
CA	Canada	KP	Democratic People's Republic of Korea	SD	Sudan
CF	Central African Republic	KR	Republic of Korea	SE	Sweden
CG	Congo	KZ	Kazakhstan	SG	Singapore
CH	Switzerland	LI	Liechtenstein	SI	Slovenia
CI	Côte d'Ivoire	LK	Sri Lanka	SK	Slovakia
CM	Cameroon	LR	Liberia	SN	Senegal
CN	China	LT	Lithuania	SZ	Swaziland
CS	Czechoslovakia	LU	Luxembourg	TD	Chad
CZ	Czech Republic	LV	Latvia	TG	Togo
DE	Germany	MC	Monaco	TJ	Tajikistan
DK	Denmark	MD	Republic of Moldova	TT	Trinidad and Tobago
EE	Estonia	MG	Madagascar	UA	Ukraine
ES	Spain	ML	Mali	UG	Uganda
FI	Finland	MN	Mongolia	US	United States of America
FR	France	MR	Mauritania	UZ	Uzbekistan
GA	Gabon			VN	Viet Nam

## THREE-PHASE EMULSION COSMETIC COMPOSITION

The present invention relates to three-phase emulsion systems and cosmetic compositions/personal wash preparations  
5 containing such emulsions. In particular, the invention relates to a rinse-off composition based on a three-phase emulsion system. The compositions according to the invention are most effective for the delivery and deposition of one or more functional ingredients on skin or hair. The invention  
10 also relates to a process for preparing the cosmetic/personal wash compositions of the present invention.

The use of functional ingredients in cosmetic compositions in order to deposit them on skin and/or hair treated therewith,  
15 is common. The common functional agents include perfumes, germicides, sunscreens and other cosmetic agents to provide specific consumer perceivable benefits. Silicone oils, usually linear poly(dimethyl siloxane) polymers of varying chain lengths and viscosities, are also employed as benefit  
20 agents for skin, hair and fabric.

The deposition of these cosmetic agents onto the substrates is aimed through leave-on or rinse-off cosmetic formulations. The problem of depositing the functional ingredients,  
25 particularly the ones which are surfactant soluble such as organic sunscreens onto the substrates especially through rinse-off cosmetic products is very pertinent as these get washed off when the composition is rinsed off.

Several attempts to enhance deposition even after rinsing  
30 have been made with varying success. There are reports (EP 0396 422 and GB 2 230 186) relating to oil-based cosmetic compositions in different forms mainly intended for leave-on products.

European Patent Specification 386 898 discloses aqueous shampoo compositions comprising anionic surfactant, a water-insoluble sunscreen material and a cationic polymer. The cationic polymer improves deposition of the sunscreen material onto treated hair, although not very significantly.

EP 0281 394 granted to Richardson-Vicks relates to a three phase emulsion of the type oil-in-water-in-silicone oil, where glycol modified silicone is used as the emulsifier for the water-in-silicone oil part of the multiphase emulsion. This emulsion is a well-defined multiple emulsion prepared by a two-stage method where a separate high HLB emulsifier is needed to first prepare the oil-in-water emulsion which is subsequently dispersed in the silicone oil by using a glycol modified siloxane. The procedure and the well defined character of the emulsion demand that a certain minimum amount of water be present and examples quoted therein show as high as 64% water content.

EP 0552 024 describes a cosmetic composition for enhanced deposition of Parsol MCX from cleanse-off application. This patent relates to an oil-in-water emulsion where the oil phase has Parsol dissolved in it. The requirement that Parsol be dissolved in the oil phase puts a restriction on the selection of the oil phase. The emulsion described is necessarily oil-in-water emulsion. There is also a restriction on the form of the final product in which these emulsions can be incorporated because of low internal phase and low viscosity of the emulsions.

Multiple phase emulsions find applications as cosmetic formulations. Out of the two major classes of multiple phase emulsions, the water/oil/water type are better known to the cosmetic industry for sometime now (there are also some commercial products in the market), and a method of preparing

these has been reported in literature, which involves a two-step procedure with a different emulsifier for each step.

5 Little knowledge exists in respect of oil/water/oil type emulsions and some special types such as oil<sub>1</sub>/oil<sub>2</sub>/water and (oil<sub>1</sub> + oil<sub>2</sub>)/water (with high internal phase), where the oils are two different immiscible oil phases.

10 Studies by the applicant reveal that such emulsions will require the stabilization of an oil/oil interface in addition in one (in case of oil<sub>1</sub>/oil<sub>2</sub>/water) or two (in case of oil<sub>1</sub> + oil<sub>2</sub>/water with high internal phase) oil/water interfaces. These, therefore, are quite complex emulsions. Multiple phase emulsions of these special types can be very effective  
15 vehicles for delivery of functional ingredients to substances.

It is an object of the present invention to provide emulsions having very little water and emulsifier content, thus  
20 minimizing the possible loss of functional ingredients in a wash situation.

It is another object of the present invention to provide a method of preparing emulsions using silicone oils of  
25 different viscosities ranging from 100 cS to 100,000 cS without sacrificing the consistency of the emulsion.

It is yet another object of the present invention to provide emulsions having enhanced occlusive properties and hence  
30 better sun-protection when the functional ingredient is a sunscreen.

It is still another object of the present invention to provide three phase emulsions having superior water-repellency and hence a longer lasting effect.  
35

It is yet a further object of the present invention to provide cosmetic compositions and method of preparing such compositions which would contain the said three phase emulsions.

5

Accordingly, in one aspect of the invention there is provided a three-phase emulsion system comprising from 2% to 30% by wt. emulsifier; from 20% to 80% by wt. one or more oil-based functional ingredients, from 2% to 30% by wt. emulsion; from 10 20% to 80% by wt. one or more oil-based functional ingredients, from 20% to 80% by wt. silicone oil and from 0.1 to 30% by wt. water, said emulsion being in a water continuous or oil-continuous form.

15

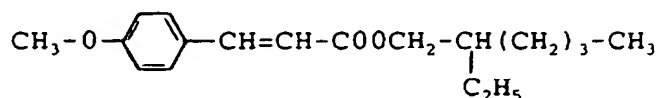
In accordance with a second aspect, the invention provides a method for preparing the three-phase emulsion as described above, comprising mixing an emulsifier with one or more functional ingredient, adding silicone fluid to the mixture, blending the mixture in a high shear mixer, adding water 20 during the mixing to obtain the emulsion.

25

In the method of the present invention the silicone oil particularly alkyl siloxanes and more particularly polydimethyl siloxanes is compatibilized with organic 25 sunscreens such as Parsol MCX (a registered trade name of Givaudan Roure) and chemically 2-ethyl-hexyl-methoxy cinnamate by way of locking the two in an emulsion. Both water-in-oil and oil-in-water emulsions can be prepared. Diversity of application to product form can be achieved by 30 altering the viscosity of the emulsion. The efficiency of deposition of the active even after the composition is rinsed off is four or five times superior to that achieved by the invention described in the prior art (EP 0 552 024).

35

The emulsion containing the functional ingredient is incorporated into the cosmetic composition for enhancing the deposition of functional ingredients such as sunscreens. More particularly, it refers to the deposition of Parsol MCX which has the following formula:



According to a third aspect, the invention provides rinse-off cosmetic compositions in particular soap bars and gels including the three-phase emulsions of the invention and method of preparation of such compositions.

The personal wash products incorporating the three-phase emulsions of the invention and functional ingredients give better deposition of the functional ingredients. The enhanced deposition is owing to a synergistic effect since silicone oil by itself does not have any UV absorbing character. The benefit in deposition of the functional ingredient on skin from bars and gels containing the three-phase emulsions.

In a method of preparation of personal wash products (soap bars and gels) containing sunscreens and/or other functional ingredient the three phase emulsions containing the functional ingredients are added to the ingredients of the personal wash products. The presence of the emulsion containing the functional ingredients results in enhanced deposition of the functional ingredient onto skin and/or hair from wash/rinse-off/cleansing products.

The cosmetic composition prepared by incorporating the novel emulsion system has a synergistic effect in the enhanced delivery of the functional ingredients. The cosmetic compositions referred to may be in the form of gels or

plodded soap bars with the emulsion containing the cosmetic agent forming stripes. The cosmetic agent may be present as stabilised droplets (50 $\mu$ ) prepared by casting the bars or may be present as a homogeneous emulsion in the composition.

5

#### FUNCTIONAL INGREDIENTS

The functional ingredient may be any surfactant-soluble material (liquid or solid) intended to be deposited onto the hair or skin for the purpose of imparting functional benefits thereto. For example, the functional ingredient may moisturise, condition and/or protect the skin and/or hair.

10

Preferred functional ingredients include:

15

- a. waxes such as carnauba, spermaceti, beeswax, lanolin and derivatives thereof;
- b. hydrophobic plant extracts;
- c. hydrocarbons such as squalene and squalane;
- d. higher fatty acids such as those having at least 12 carbon atoms, for example, lauric, myristic, palmitic, stearic, behenic, oleic, linoleic, linolenic, lanolic, isostearic and polyunsaturated fatty acids (PUFA) acids;
- e. higher fatty alcohols such as those having at least 12 carbon atoms, for example, lauryl, cetyl, stearyl, oleyl, behenyl, cholesterol and 2-hexadecanol alcohol;
- f. esters such as cetyl octanoate, lauryl lactate, myristyl lactate, cetyl lactate, isopropyl myristate, myristyl myristate, isopropyl palmitate, isopropyl adipate, butyl stearate, decyl oleate, cholesterol isostearate, glycerol monostearate, glycerol distearate, glycerol tristearate, alkyl lactate, alkyl citrate and alkyl tartrate;
- g. essential oils such as fish oils, mentha, jasmine, camphor, white cedar, bitter orange peel, ryu,

20

25

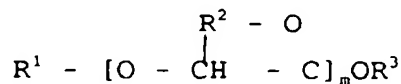
30

35



turpentine, cinnamon, bergamont, citrus unshiu, calamus, pine, lavender, bay, clove, hiba, eucalyptus, lemon, starflower, thyme, peppermint, rose, sage, menthol, cineole, eugenol, citral, citronelle, borneol, linalool, geraniol, evening primrose, camphor, thymol, spirantol, pinene, limonene and terpenoid oils;

- h. lipids such as cholesterol, ceramides, sucrose esters and pseudo-ceramides as described in European Patent Specification No. 556 957;
- i. vitamins such as vitamins A and E, and vitamin alkyl esters, including vitamin C alkyl esters;
- j. sunscreens such as octyl methoxyl cinnamate (Parsol MCX) and butyl methoxy benzoylmethane (Parsol 1789);
- k. Phospholipids; and
- l. derivatives of alpha hydroxy acids such as materials of formula



wherein,

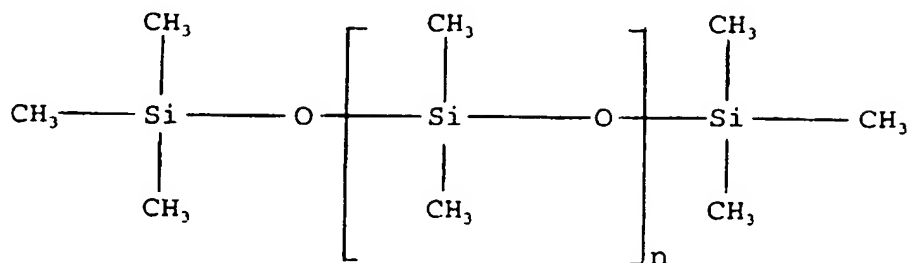
- R<sup>1</sup> is C<sub>p</sub>H<sub>q</sub>N<sub>r</sub>O<sub>s</sub>, where P is 0-20, q is 1-41, r is 0-3, and S is 0-3;
- R<sup>2</sup> is C<sub>t</sub>H<sub>u</sub>, where t is 0-20 and u is 1-41;
- R<sup>3</sup> is C<sub>v</sub>H<sub>w</sub>N<sub>x</sub>O<sub>y</sub>, where v is 0-20, w is 1-41, x is 0-3 and y is 0-3 or a metallic, ammonium or alkanolammonium anion; and m is 1-10;
- m. perfumes; and
- n. mixtures of any of the foregoing components.

The invention will be described hereinafter in further detail with reference to a sunscreen as the functional ingredient.

The functional ingredients are present in the emulsions preferably in amounts of from 20% to 80%, more preferably from 40% to 60%.

SILICONE OIL

Silicone oils have the following formula:



They have different viscosities which increases with increasing  $n$ , the degree of polymerization. The silicone oil is present in the emulsion preferably in an amount of from 20% to 80%.

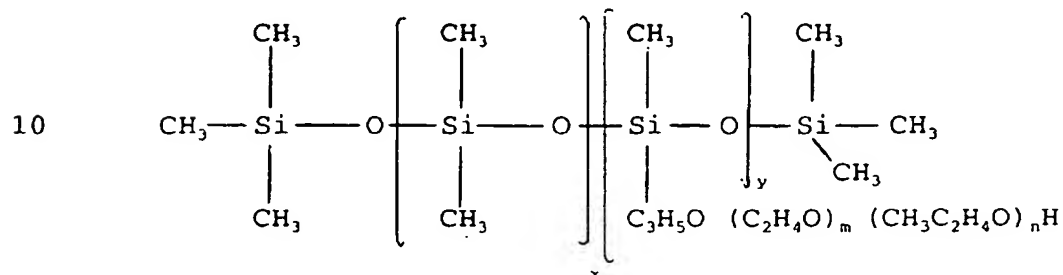
WATER

Water is incorporated as the third phase of the three-phase emulsions and may be incorporated in one or more stages during emulsifications. Water is present in the emulsion in amount of between 0.1% to 30%, more preferably from 5 to 15%.

EMULSIFIER

The known HLB guidelines for selection of emulsifier for making oil-in-water or water-in-oil type of emulsions do not work when the question of compatibilization of two immiscible oils is faced. If small amounts of the two oils need to be co-emulsified in water (for example in most cosmetic creams), one could still find out a weight average of the required HLB's and use that as a guide. However, if the relative proportions of the two oils are large enough (which is the case in HIPE described in this invention) then there has to be a stable interface between two oils in the final emulsion.

The emulsifier should on one part have affinity for silicones and on other part have affinity for the oils in question. A wide range of modified siloxanes are commercially available. Glycol modified siloxanes (from Dow Corning) of the formula shown below may be used for the purpose of the present invention:



The relative proportions of the siloxane groups and the polyol groups in the copolymer determines the character of the emulsion that can be obtained. DC 190 has a lower glycol content than DC 193 and hence leads to water as the internal phase in the emulsions. DC 190 and DC 193 are brand names of Dow Corning in respect of the aforesaid siloxanes. The emulsifiers are present in the emulsion preferably in amounts from 2 to 30% by wt., more preferably from 5 to 15% by wt.

#### EMULSION PREPARATION

In the method of preparation of three-phase emulsions the emulsifiers are first dispersed in one or more functional ingredient and slightly heated, if required. This is followed by addition of silicone oil and mixing in a high shear mixer such as the ones available from Silverson. Water and minor additives are then added slowly while mixing is continued. As water is added, the viscosity starts building up and the required consistency of the emulsion is obtained. Thus, a simple one-step mixing procedure can be used to

prepare a three-phase emulsion (hereinafter referred to as Parsol-Silicone-Emulsions [PSE]).

The character of the emulsion was tested by dispersing a small drop of the emulsion in test tubes containing water and oil phases separately. The emulsion can be easily dispersed (and hence diluted) in a medium which constitutes the external phase whereas it forms lumps in the other fluids.

#### Water-continuous PSE formulation

A typical water continuous PSE formulation is as follows:

Parasol MCX	40 gms
DC-193	10 gms
Silicone oil (PDMS)	60 gms
Water	10 gms
Minors	0-10 gms

#### Oil-continuous PSE formulation

A typical oil continuous PSE formulation is as follows:

Parasol MCX	40 gms
DC-190	10 gms
Silicone oil (PDMS)	60 gms
Water	10 gms
Minors	0-10 gms

The minors will include:

1. particulates such as ppt. silica, talc and high HLB non-ionics preferably the ones which form liquid crystalline phases at interfaces, such as the ethoxylated stearyl alcohol, e.g., Brij 72/BVrij 721 (registered trade mark of TCI).
2. materials for added benefits such as niacinamides, microfined ZnO, TiO<sub>2</sub>, etc.

The emulsions themselves offer synergy by combining the benefits of sunscreen and silicone oil. They may be used as such (without further incorporation into a product) as a pre-wash/cleansing cream which is applied on face and later washed off leaving the sunscreen on the face.

#### COSMETIC COMPOSITIONS

The three-phase emulsions of the invention containing the functional ingredients may be used in personal washing bars and gels. PSE's may be incorporated into gel type products in the form of stripes, and into soap bars either in the form of stripes (for plodding route) or as big droplets (for casting route). Parasol MCX alone cannot be striped on gels and bars and also runs the risk of getting solubilized by the surfactant micelles during application of the product. In the case of melt cast route of making soap bars, silicone oil alone cannot be stabilized in the form of large droplets while Parsol alone does not give the desired substantivity. Large drops of PSE's are easy to stabilize in the soap melt. Thus, synergistic benefits can be obtained by combining Parsol and silicones in the form of PSE's not only in terms of depositing Parsol but also in terms of the ease of processing.

The invention will now be described with reference to non-limiting examples.

For the purpose of the various experiments of the invention  
5 Silicone oils (poly dimethyl siloxanes) of 60,000 cS and  
350 cS viscosities obtained from Reliance Silicones were  
used. Glycol modified siloxane surfactants (DC-193 and  
DC-190) of Dow Corning (USA) and Parsol MCX, cosmetic grade  
10 sunscreen were used.

#### EXAMPLE I

##### WATER CONTINUOUS HIGH-INTERNAL-PHASE-EMULSIONS (HIPE's)

15 A total of 6 emulsions being emulsion nos. 1 to 6 (Table 1)  
were prepared by the following method:

The emulsifier (10 gms) was mixed in Parsol MCX (50 gms) in a  
150 ml glass beaker and then silicone fluid (60 gms) was  
20 added to the mixture. The mixture was heated to about 50°C  
in a water bath and then subjected to high shear mixing on  
Silverson mixer. When the mass became somewhat uniform on a  
macroscopic scale, the required amount of water (typically  
10 gms) was added slowly while mixing in the Silverson was  
25 continued. As the water was added, a sudden build-up in the  
viscosity of the mass was observed with the whitening of the  
mass. This indicated the onset of emulsification. Mixing  
was continued for another 5 minutes to homogenize the  
emulsion.

30 The emulsion nos. 1 to 6 of Table 1 will lead to an internal  
phases of ~100 gms on an external phase of only 10 gms if  
water forms the continuous phase. Hence they come under the  
category of high internal phase emulsions (HIPE's) in which  
35 the internal phases are no longer in the form of discrete

droplets. They are instead deformed and pressed against one another. Since the system has already passed the limit of internal phase that can be accommodated assuming hard spheres (~74%), the viscosity is extremely high. These emulsions offer excellent materials for striping Parsol-rich material on gel type products.

#### PHASE-STRUCTURE

The emulsions are easily dispersed in bulk water indicating that the continuous phase is water. However, since the total amount of water is very small (10%), their structure will look like the one shown in the schematic of Figure 1 with the oil phase consisting of two components (Parsol and Silicone). The emulsions being very thick, they cannot be examined under an optical microscope as such. Therefore, they were diluted 20 times before looking at them under the microscope. Figure 2 shows a microscope picture at 400 magnification. Two distinct type of oil droplets can be seen in the picture which might be interpreted to correspond to two oil phases. Although not very clear in the picture, the visual inspection under the microscope also shows evidence of some drops containing one oil inside the other. These, however, coalesce very fast under the diluted conditions and it was not possible to take a picture.

Figure 3 shows a typical droplet size distribution for these emulsions obtained by dispersing a small amount of the emulsion in water and counting the droplets on a Coulter Multisizer. The average droplet size is seen as ~15 microns and the distribution is quite broad. However, while trying to interpret these results, one must bear in mind that the character of a high internal phase emulsion gets significantly altered once it is diluted since there is no inter-droplet interaction or dense packing left after

dilution. A fast coalescence may lead to over-estimation of the droplet size by this technique.

### STABILITY

5

10

15

20

25

30

35

Stability of high internal phase emulsions is a critical issue since the total interfacial area to be stabilized with the emulsifier is very high and the external bulk phase is very thin layer through which the droplets have to travel in order to coalesce. However, the inherent high viscosity of these emulsions, which renders them a pasty look, acts favourably. Two separate procedures were used to study the stability of these emulsions under accelerated storage conditions. In one case, the emulsion samples nos. 1 to 6 shown in Table 1 were filled in small glass bottles (~1 cm in diameter and 4 cm high) and kept in an oven maintained at 50°C. Periodically, the condition of the emulsions was assessed and assigned a number (1-stable, 2-slight oil oozing out on top, 3-fair amount of separation, 4- complete separation). Three months of storage at 45-50°C is usually equivalent to one year of storage at 20-25°C for most emulsion systems. In the other method, the emulsions were subjected to accelerated gravity by high speed centrifugation. One hour long centrifugation action at 8000 rpm for a sample kept at 6 cm arm distance from the centre is equivalent to 6 months of storage under gravity. Table 1 summarizes our results on an accelerated storage test based on temperature and Table 2 summarizes similar results on the accelerates stability test based on centrifugation. Although an elaborate stability study was carried out, only a few good ones are listed in these tables. It can be seen that, in general, the emulsions with silicone oil of lower viscosity (350 cS) are more stable than those prepared with high viscosity (60,000 cS) oil. This could possibly be attributed to the ease of emulsification of the lower viscosity oil to



smaller droplets which lead to a more stable emulsion. The basic formulation with high viscosity silicone is not so stable as such, however, it can be made more stable by increasing the amount of DC 193 from 10 gms to 15 gms.

Adding cationic polymer Jaguar at 1% level to the water phase (based on the water quantity) helps stabilize the emulsion at room temperature but it worsens the stability at high temperature. In general, most of our emulsions have passed the stability criterion by centrifugation method. In brief, we have been able to prepare emulsions which are stable over more than three months at 50°C indicating that they may be stable for almost a year at room temperature in the sample vials used in our testing method.

## EXAMPLE II

### OIL-CONTINUOUS PARSOL-SILICONE-EMULSIONS

DC 190 has a relatively lower glycol content in the silicone glycol copolymer, and is more suitable for making an oil-continuous emulsion. A similar experiment as in Example I, with DC 190 in place of DC 193 was used to prepare emulsions with water as one of the internal phases. A typical recipe is given below:

Parsol MCX	40 gms
DC 190	10 gms
Silicone oil	60 gms
Water	10 gms

### PHASE-STRUCTURE

The emulsions do not disperse in water and instead form lumps. This indicates that the continuous phase is an oil phases in this case. Figure 4 shows an optical microscope picture of an oil-continuous PSE taken without any dilution. The slide was prepared by putting a drop of the emulsion onto the slide, cover it with a cover slip and pressing it hard with thumb. As can be seen, the continuous oil phase spreads into irregular domains with the two types of droplets dispersed in them. On the whole, the picture exhibits a very different character than the one in Figure 2.

### STABILITY

The very fact that they have much lower internal phase ratio than their water-continuous counterparts, implies that they are going to be more stable and as such the stability of these emulsions is not an issue.

### EXAMPLE III

#### STRIPED BARS

Known dye injection technology was used for making striped bar prototypes on pilot plant. A metered amount of the emulsion was injected into the cone of the plodder using a metering pump and a special pressure plate in the plodder which is fitted with six nozzles to inject the striping material. Two different base formulations used in this case were: (i) 78 TFM with 1.2% perfume and 0.5%  $\text{TiO}_2$ , and (ii) 55 TFM with 12% kaolin, 12% talc, 0.5%  $\text{TiO}_2$ , and 1.2% perfume.

EXAMPLE IVMELT-CASE-BARS

5 A typical transparent soap formulation containing 30% soap,  
40% polyols, 20% water and 10% ethyl alcohol was taken. A 2  
kg batch of melt was prepared, cast into moulds, and tablets  
were cut out on solification. Later, a few of these were  
remelted and cooled to a lower temperature around 50°C) while  
10 continuously stirring the mass not to allow localized  
solidification. This was done to achieve a higher viscosity  
of the melt which facilitates the stabilization of droplets.  
At this stage, an appropriate amount of PSE was added to the  
viscous (but still liquid) mass. The system was homogenized  
15 by gently stirring by hand for about 5 minutes and then cast  
in pre-cooled moulds (kept in refrigerator). Bars were cut  
after solidification.

EXAMPLE V

20

STRIPED GELS

The following formulation of wash gel was taken:

25	K-CNFA soap	:	10%
	K-stearate	:	25%
	Glycerine	:	10%
	Water	:	50%
	Minors	:	5%

30

Small size (50 gms) plastic toothpaste tubes as shown in  
Figure 5 were taken. Prototypes were prepared by filling the  
tubes manually. First a Parsol containing striping emulsion  
was filled in the lower zone of the tube followed by the base  
35 formulation on top. The tubes were then sealed. On

squeezing the tubes, a well formed ribbon of the base formulation is extruded out with stripes of the Parsol-rich emulsion sticking to the surface.

5     EXAMPLE VI

DEPOSITION FROM STRIPED BARS

10     Samples of emulsion nos. 7 to 10 according to the invention were prepared, as in Example 1 but using the appropriate amounts of ingredients, and these are shown in Table 4. Emulsion no. 7 was injected at ~1% level to give stripes on a 55 TFM soap formulation. A corresponding control was prepared by mixing the equivalent amount of Parsol mixture 15     (MCX/1789 = 80/20) and silicone oil as such to the sigma mixer followed by plodding and stamping.

20     For the purpose of in-vitro testing, the procedure involved prewashing the forearms, applying 20 to-and-fro rubs of the experimental soap on one inner forearm, lathering for ~10 seconds, rinsing, and drying by tapping paper towel. Similar application of the control was carried out on the other forearm. This was followed by the extraction of the deposited Parsol MCX using 400 microlitres of ethanol from 9 25     cm<sup>2</sup> are marked on each forearm, and determining the amount of Parsol using UV. The results are shown in Table 5. The results clearly indicate that the deposition from the striped bar prepared as per the invention is significantly higher than from the control bar at 99% statistical confidence 30     level. The control bar has both Parsol and Silicone in the same proportions as in the striped bar but without emulsification. This clearly shows the benefit of the two ingredients being locked together in the form of PSE coupled with the striping. This kind of deposition figures from 35     striped bars have not been obtained earlier.

EXAMPLE VIIDEPOSITION FROM MELT-CAST-BARS

5 Table 6 shows the deposition of Parsol MCX respectively from melt-cast-bars containing 2% Parsol incorporated (i) as neat (sample No. MCB-13), (ii) via a water-continuous emulsion, being emulsion no. 9 (sample no. MCB-14), and (iii) ia oil-continuous emulsion, being emulsion no. 8 (sample no. MCB-10 15). The measurements were made by making a 1% solution of the soap bars in water, applying 100 microlitres of this solution on the forearms of the subjects, and then following similar procedure as described. From the deposition values it follows that:

15

- i) the deposition from the bars containing droplets of Parsol as such is quite high which implies that the melt-cast method itself has a benefit.
- 20 ii) the deposition figures are further improved significantly when Parsol is incorporated as PSE, whether water-continuous or oil-continuous, implying the synergistic effects of the Parsol and silicone being present together in the form of an emulsion. It is 25 significant that silicone alone cannot be stabilized at droplets in the melt. Due to its lower density it quickly float on the top.

It may be noted that a test like the one above where the application involves making a solution from the bar is 30 generally not applicable for striped bars. However, with the melt-cast-bars containing Parsol, it can still be considered valid because the number of droplets of 100 microns average

diameter present in 100 microlitres (the applied volume) are as many as  $2 \times 10^5$ . Thus, the inhomogeneity in the product is on a much smaller scale and does not affect the measurements.

5       Following the above observations, yet another test was carried out exactly on the lines of the test performed for striped bars where the bar was directly applied 20 rubs to-and-fro instead of making a solution of it. The results are shown in Table 7. These results further strengthen our  
10       earlier interpretation that locking Parsol and silicone in a three-phase emulsion offers synergistic benefit.

#### EXAMPLE VIII

#### 15       DEPOSITION FROM STRIPED GELS

Although product prototypes were made with PSE striped on face wash gel dispensed from a squeeze tube, deposition could not be tested directly by using the striped gel since  
20       monitoring the amount of ribbon delivered by squeezing tube was found to be difficult. Therefore, an experiment was conducted where one drop (weighing ~0.04 gms) of emulsion no. 10 was applied on one forearm followed by the application of face wash base (0.6 gms delivered as a certain length of the ribbon from a plastic syringe) to give Parsol as 2% in the  
25       product. The formulation of the face wash base is given in Example VI. The total mass was then rubbed together, lathered, rinsed and wiped dry. On the other forearm, same amount of control (2% Parsol MCX uniformly mixed in the base)  
30       was applied. The extraction was done following the same procedure as in Example VII. Table 8 shows that deposition figures in the two situations. The results show that the deposition from the simulated striped gel is significantly higher than that from a gel containing Parsol uniformly mixed  
35       at the same level. In this case, the advantage of using

Parsol by way of PSE is far more significant compared to the earlier two case, i.e., from the striped bars and melt-cast-bars.

5      Table 1

Ingredient (parts by wt.)	Emulsion No.					
	1	2	3	4	5	6
Parsol MCX	40	40	40	40	40	40
DC-193	10	10	10	10	10	15
Silicone (350)	60	60	60	-	-	-
Silicone (60,000)	-	-	-	60	60	60
Water	10	10	-	10	10	10
Water (1% Jaguar)	-	-	10	-	-	-
Brij 72*	-	5	-	-	5	-
Rating** after three months storage at Room Temp.	1	1	1	1-2	1	1
Rating** after three months storage at 50°C	1	1	1	1-2	1	1

\* Registered Trade Mark of ICI

\*\* 1 : Stable; 2 : Slight oil oozing out on top

Table 2Accelerated Storage Testing by Centrifugation

5 (8000 rpm at distance of 6 cm from the centre)

Emulsion No.	Rating* after		
	¼ hr	1 hr	1½ hr
1	1	1	1
2	1	1	1
3	1	1	1
4	1	1	1
5	1	1	1
6	1	1	1
7	1	1	1

\* Rating: 1 - Stable

2 - Slight oil oozing on top

Table 3Cohesivity Values

Emulsion No.	C.V.
1	240
2	260
3	480
4	310
5	250
6	270



Table 4

Ingredient (% by wt.)	Emulsion No.			
	7	8	9	10
Parsol MCX		33.33	33.33	33.33
Parsol Mix (MCX/1789 = 80/20)	50			
DC-190	8.33	8.33		8.33
DC-193			8.33	
Silicone (60,000 CS)	33.33	50	50	50
Water	8.33	8.33	8.33	8.33
Colour Pigment	q.s.			
Water continuous emulsion (W)			W	
Oil continuous emulsion (O)	O	O		O

Table 5

Deposition of Parsol Mix from Striped Bars  
 (Total Parsol level in the bars = ~0.5%)

Protocol: 20 to-and-fro rubs of the bar on prewashed inner forearm, lather for 10 seconds, rinse, tap dry, extraction with 400 microlitres of alcohol from 9 cm<sup>2</sup>

Panellist	Deposition (micrograms/9 cm <sup>2</sup> )		
	Experimental	Control	Difference
1	5.813	4.625	1.188
2	5.313	2.325	2.988
3	6.600	4.175	2.425
4	7.313	4.488	2.825
5	3.600	2.300	1.300
6	8.163	8.113	0.050
7	3.838	2.388	1.450
8	7.075	4.713	2.362
9	2.863	2.075	0.788
10	3.725	0.119	3.606

THE DIFFERENCE (1.9 microgram/9 cm<sup>2</sup>) IS STATISTICALLY  
SIGNIFICANT AT 99% CONFIDENCE LEVEL

Table 6

Deposition of Parsol MCX from Melt-Cast-Bars (MCBs)  
(Application : 100 microlitres of 1% product solution on  
9 cm<sup>2</sup>)

Protocol: Application of 100 microlitres of 1% solution of  
the product on prewashed inner forearm, lather for  
10 seconds, rinse, tap dry extraction with 400  
microlitres of alcohol from 9 cm<sup>2</sup>

	Parsol Deposition (micrograms/9 cm <sup>2</sup> )
MCB-13 2% Parsol MCX added as neat	5.63
MCB-14 2% Parsol MCX added via Water-Continuous PSE	9.10
MCB-15 2% Parsol MCX added via Oil-Continuous PSE	8.22

C.D. = 2.10

Table 7Deposition of Parsol MCX from Melt-Cast Bars (MCBs)

Protocol: 20 to-and-fro rubs of the bar on pre-washed inner forearm, lather for 10 seconds, rinse, tap dry, extraction with 400 microlitres of alcohol from 9 cm<sup>2</sup>

MCB-13: 2% Parsol MCX added as neat.

MCB-14: 2% Parsol MCX added via Water-Continuous PSE.

Panellist	Deposition (micrograms/9 cm <sup>2</sup> )		
	MCB-14	MCB-13	Difference
1	14.87	10.73	4.44
2	22.23	19.42	2.81
3	34.53	34.00	0.53
4	19.56	10.85	8.73
5	19.46	16.05	3.41
6	15.38	14.92	0.46
7	14.86	9.85	2.01
8	16.22	10.33	5.89
9	22.16	11.12	11.04
10	10.19	11.66	-0.75

Average: 4.05

THE DIFFERENCE (4.05 micrograms/9 gm<sup>2</sup>) IS STATISTICALLY  
SIGNIFICANT AT 99% CONFIDENCE LEVEL

Table 8Deposition of Parsol MCX from Striped Gels

Experimental: 2% Parsol MCX via Oil-Continuous PSE applied  
separately

Control: 2% Parsol MCX mixed uniformly into the base

Panellist	Deposition (micrograms/9 cm <sup>2</sup> )		
	Experimental	Control	Difference
1	31.54	9.29	22.25
2	11.81	7.81	4.0
3	18.62	6.26	12.36
4	15.50	5.82	9.68
5	20.86	6.45	14.41
6	14.18	6.41	7.77
7	8.16	6.74	1.42
8	28.61	13.86	14.75
9	19.72	8.49	11.23

Average: 10.88

THE DIFFERENCE (10.88 micrograms/9 cm<sup>2</sup>) STATISTICALLY  
SIGNIFICANT AT 99% CONFIDENCE LEVEL

**CLAIMS**

1. A three-phase emulsion system comprising from 2% to 30% by wt. emulsifier; from 20% to 80% by wt. of one or more oil-based functional ingredients; from 20% to 80% by wt. silicone oil; and from 0.1% to 30% by wt. water; said emulsion being in a water continuous or oil-continuous form.
2. A three-phase emulsion system as claimed in Claim 1, comprising from 40% to 60% by wt. of the functional ingredient(s).
3. A three-phase emulsion system as claimed in either Claim 1 or Claim 2, comprising from 5% to 15% by wt. of water.
4. A three-phase emulsion system as claimed in any preceding Claim, comprising from 5% to 15% by wt. of the emulsifier.
5. A three-phase emulsion system according to any preceding Claim, wherein the silicone oil is an alkyl siloxane, preferably a polydimethyl siloxane.
6. A rinse-off cosmetic composition comprising the three-phase emulsion system according to any preceding Claim.
7. A rinse-off cosmetic composition according to claim 6 in the form of a soap bar or gel.
8. A method for preparing the three-phase emulsion system of any of Claims 1 to 5, comprising mixing an emulsifier

with one or more functional ingredient, adding silicone fluid to the mixture, blending the mixture in a high shear mixer, and adding water during the mixing to obtain the emulsion.

Fig.1.

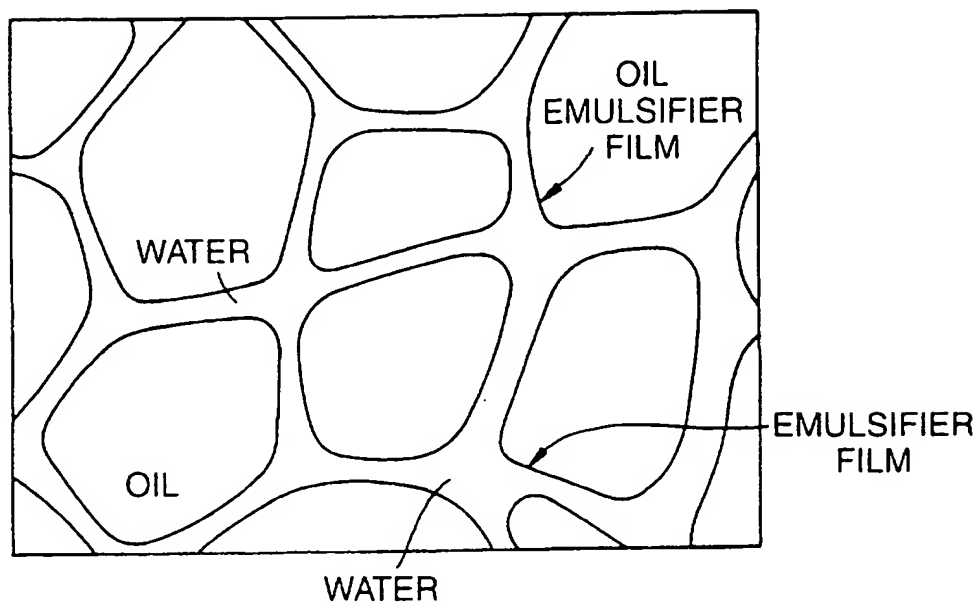



Fig.3.

SAMPLE: 1      256 CHANNEL FULL RANGE      COULTER@  
X-AXIS(ACC. LAW): Lin Dia.      MULTISIZER II  
Y-AXIS(DISPLAY): Volume Cum>      20/09/94  
BLANK SUBTRACT: 

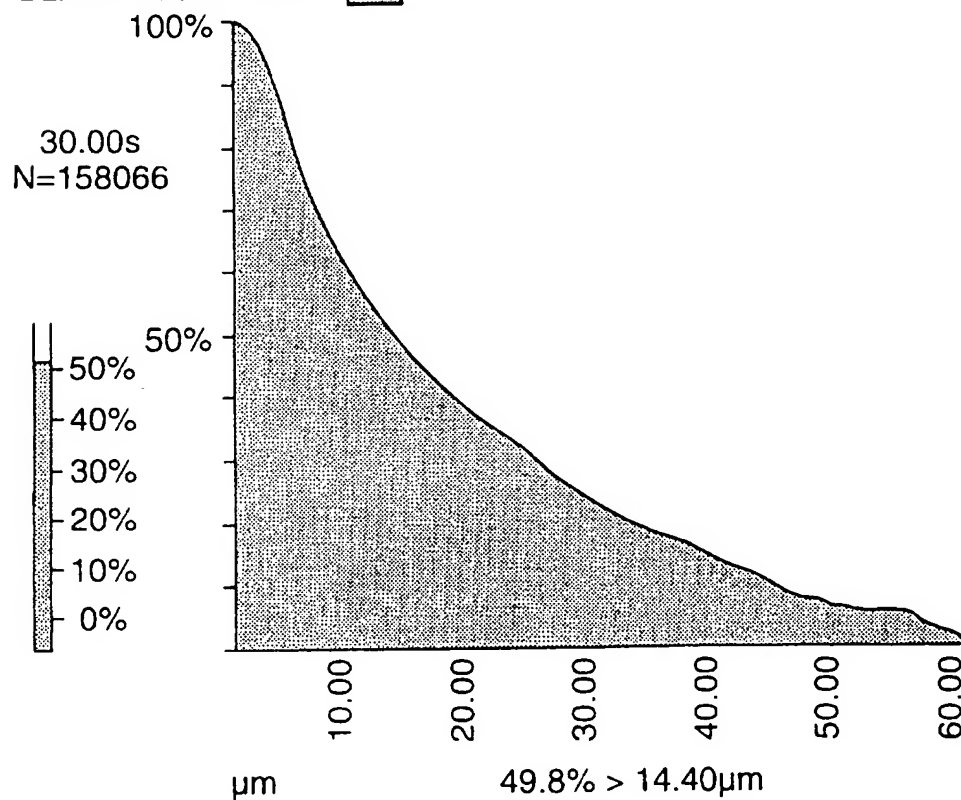




Fig.2.

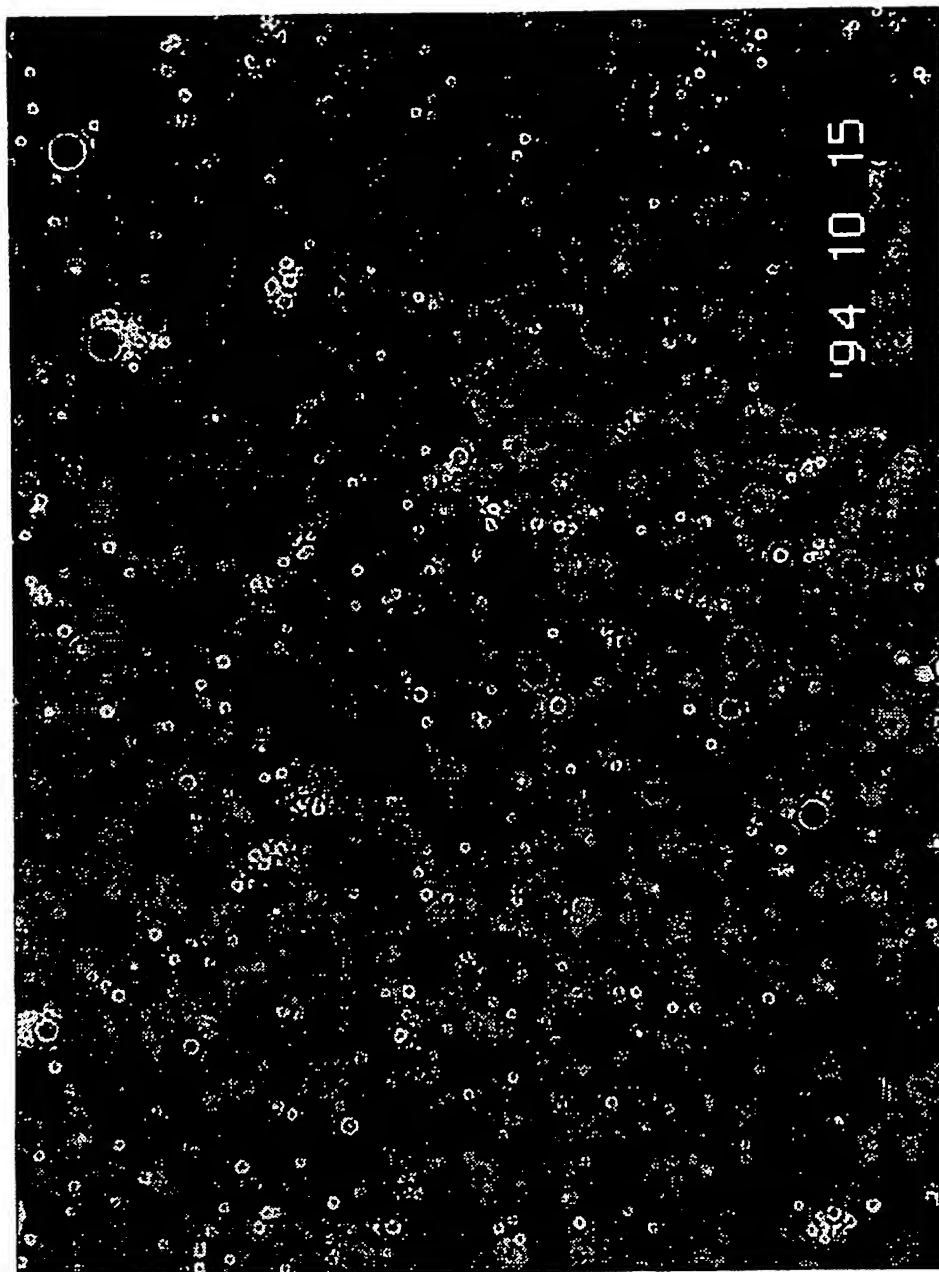
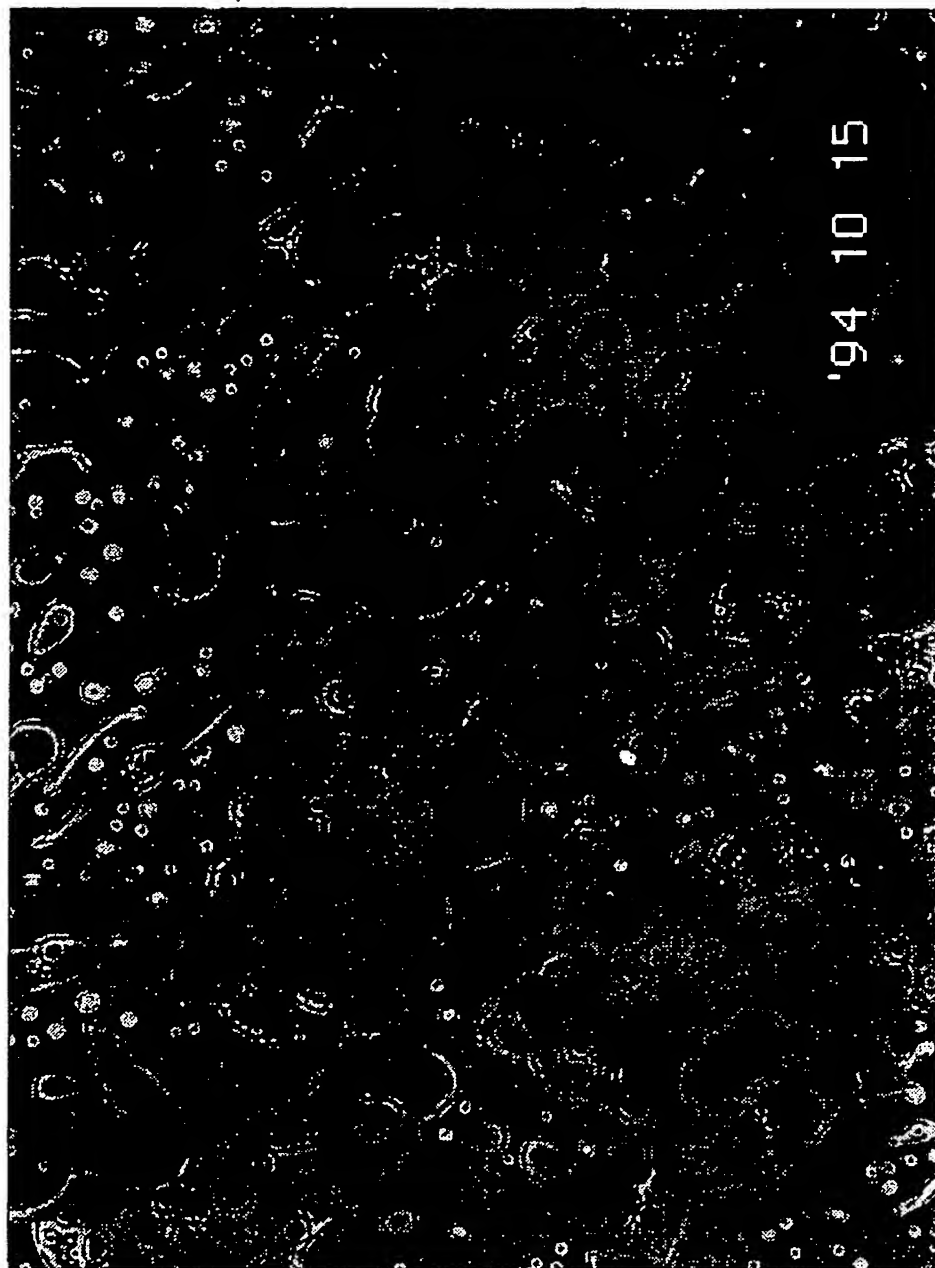
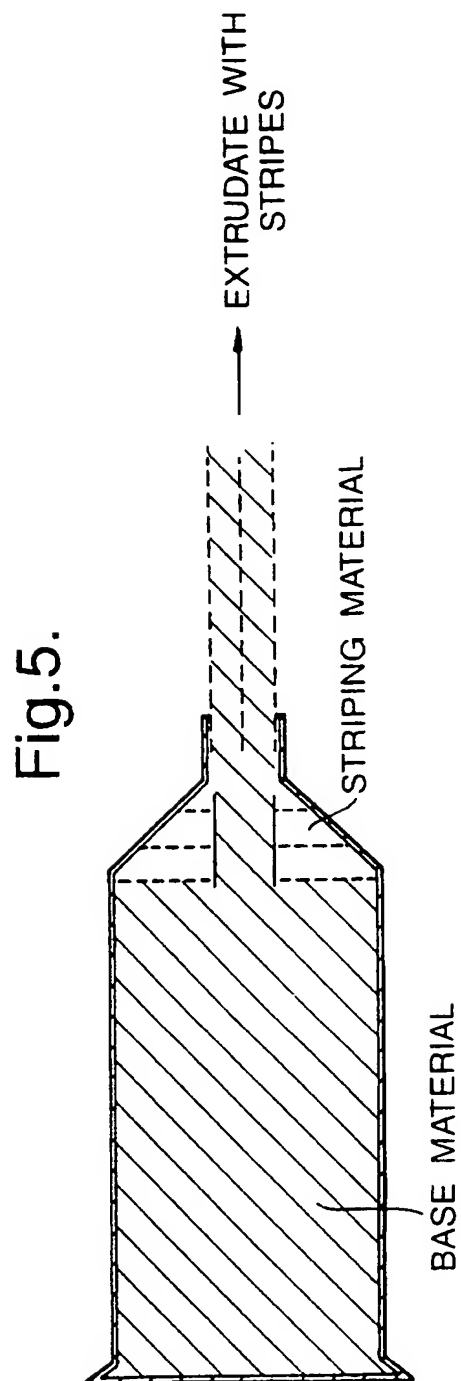


Fig.4.





## INTERNATIONAL SEARCH REPORT

International Application No  
PCT/EP 96/04172

A. CLASSIFICATION OF SUBJECT MATTER  
IPC 6 A61K7/00 C11D17/00

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)  
IPC 6 A61K C11D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	CHEMICAL ABSTRACTS, vol. 123, no. 6, 7 August 1995 Columbus, Ohio, US; abstract no. 65564, K. ONIZUKA: "multilayered oil-water-oil type emulsion cosmetics containing UV absorbents" XP002027089 see abstract & JP 07 101 844 A (SANSEI SEIYAKU KK) 18 April 1995	1-8
A	EP 0 330 369 A (RICHARDSON VICKS INC) 30 August 1989 see the whole document	1-8
A	EP 0 391 124 A (KAO CORP) 10 October 1990 see the whole document	1-8
-/-		

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

## \* Special categories of cited documents:

- \*A\* document defining the general state of the art which is not considered to be of particular relevance
- \*E\* earlier document but published on or after the international filing date
- \*L\* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- \*O\* document referring to an oral disclosure, use, exhibition or other means
- \*P\* document published prior to the international filing date but later than the priority date claimed

\*T\* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

\*X\* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

\*Y\* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

\*G\* document member of the same patent family

Date of the actual completion of the international search

21 March 1997

Date of mailing of the international search report

04.04.97

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2  
NL - 2280 HV Rijswijk  
Tel. (+ 31-70) 340-2040, Tx. 31 651 epo nl,  
Fax (+ 31-70) 340-3016

Authorized officer

Sierra Gonzalez, M

# INTERNATIONAL SEARCH REPORT

Int:      nal Application No  
PCT/EP 96/04172

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 0 396 422 A (UNILEVER PLC ;UNILEVER NV (NL)) 7 November 1990 cited in the application see the whole document ---	1-8
A	EP 0 552 024 A (UNILEVER PLC) 21 July 1993 cited in the application see the whole document -----	1-8

# INTERNATIONAL SEARCH REPORT

International Application No

PCT/EP 96/04172

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 0330369 A	30-08-89	AU 2998289 A JP 1287008 A	17-08-89 17-11-89
EP 0391124 A	10-10-90	AT 123937 T DE 69020211 D DE 69020211 T JP 3047108 A	15-07-95 27-07-95 02-11-95 28-02-91
EP 0396422 A	07-11-90	CA 2015867 A,C DE 69006902 D DE 69006902 T ES 2062357 T JP 3020207 A	05-11-90 07-04-94 30-06-94 16-12-94 29-01-91
EP 552024 A	21-07-93	AU 3181393 A AU 6562896 A BR 9300143 A CA 2087140 A JP 5279232 A ZA 9300269 A	22-07-93 07-11-96 27-07-93 16-07-93 26-10-93 15-07-94